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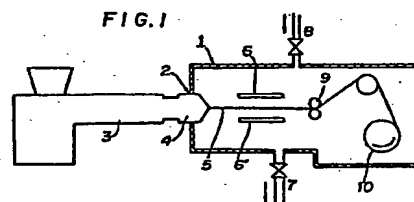
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⑤④ A method for the treatment of a thermoplastic resin.

⑤⑦ The invention provides a very efficient method for improving the surface properties, e.g. hydrophilicity, susceptibility to adhesion, printability, etc., of a thermoplastic resin article. The inventive method comprises subjecting the surface of the thermoplastic resin to a vacuum plasma treatment while the resin is kept at a temperature equal to or higher than the melting or softening point of the resin. Further, the thermoplastic resin in the form of a sheet or film after the vacuum plasma treatment is subsequently laminated with another material of a different kind of material to prepare a laminated material, which has an unexpectedly high adhesive bonding strength between layers.



A METHOD FOR THE TREATMENT OF A THERMOPLASTIC  
RESIN

BACKGROUND OF THE INVENTION

The present invention relates to a method for the treatment of a thermoplastic resin or, more particularly, relates to a method for the treatment of a thermoplastic resin with an object to impart improved properties thereto characterized in the vacuum plasma treatment of the resin at a specified temperature.

Needless to say, thermoplastic resins have excellent properties and are easily moldable in general so that they are widely used in a variety of application fields. Thermoplastic resins represented by polyolefins are, however, poor in the adhesion susceptibility, paintability, printability, plating adaptability, wearing resistance, antistatic performance and the like properties due to their low polarity so that these resins are sometimes subjected to a certain surface treatment with an object to improve the surface properties thereof in these respects.

Known methods for the surface treatment of thermoplastic resins include a wet-process treatment with a chromic acid mixture, corona discharge treatment, flame treatment and the like. The treating method using a chromic acid mixture, however, has a problem in the disposal of the spent acid solution and the other methods are not free from the inherent problem that the types of the thermoplastic

resins to which the method is applicable are limited.

Alternatively, a method for the modification is known by the graft polymerization of an unsaturated carboxylic acid or a derivative. This method is, however, performed in a complicate process so that the resin prepared by the method are unavoidably expensive. When the method is performed under melting of the resin, in addition, a part of the unsaturated carboxylic acid or the derivative thereof is always left unreacted and must be removed with additional costs.

In view of the above problems, one of the recently developed promising methods for the treatment of a thermoplastic resin in the above mentioned object is the method of vacuum plasma treatment. It has been proposed in Japanese Patent Kokai 57-115431 that the vacuum plasma treatment of a thermoplastic resin article for surface improvement can be performed with high efficiency by keeping the surface temperature of the resin article at a relatively high temperature of from 40 to 100°C. A problem in this method is that the treatment temperature should be lower by at least 10°C than the melting or softening point of the resin under treatment in order to avoid deformation of the shaped article of the thermoplastic resin.

Since the method of the vacuum plasma treatment is a dry process undertaken in a high vacuum, the method requires a hermetically sealable vacuum-tight apparatus. Therefore, the method is conventionally performed in a batch-wise process so that a great difficulty is encountered when the

method is practiced in an industrial scale. Various methods and apparatuses have been proposed in order to solve these problems accordingly. For example, Japanese Patent Kokai 57-67636 discloses a method and apparatus for the continuous plasma treatment in which the plasma treatment chamber is provided at the front and at the rear with a plural number of zones each under a vacuum pressure differing in a stepwise manner from the adjacent ones. Further, Japanese Patent Kokai 57-18737 discloses an apparatus for the continuous plasma treatment in which the material under treatment is introduced into the plasma chamber from the open air through a front preparatory vacuum chamber and, after completion of the plasma treatment, continuously brought out to the open air through a rear preparatory vacuum chamber.

In each of these prior art methods and apparatuses, however, the plasma treatment chamber must be provided with two sealing devices to the atmosphere at the inlet port and outlet port of the material so that the apparatus is unavoidably expensive resulting in a high cost for the plasma treatment. In addition, it is usually difficult to provide a heating means of the material with an object of increasing the effectiveness of the treatment, in particular, with no possibility of heating at the softening point of the resin or higher. Moreover, the films, sheets and the like materials before the plasma treatment are subject to ready contamination with dusts, dirt, fungi and the like deposited thereon which can be prevented only by use of

elaborate equipments.

When a laminated material is prepared using sheets of two kinds or more of different thermoplastic resins or sheets of a thermoplastic resin and another kind of material in combination, on the other hand, these sheets are bonded together by use of an adhesive or they are co-extruded together with an adhesive resin sandwiched therebetween. The problems in these methods are the essential use of an adhesive as the third component and the necessity of an extrusion equipment for the adhesive resin.

#### SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a novel method for the treatment of a thermoplastic resin freed from all of the above described problems and disadvantages in the prior art methods.

Another object of the invention is to provide a method for the preparation of a laminated material utilizing the above mentioned treatment method of a thermoplastic resin.

That is, the first of the objects of the present invention is to provide a novel treatment method for obtaining a thermoplastic resin imparted with various improved physical properties.

The second object of the present invention is to provide an economically advantageous and efficient method for the preparation of a laminated material by the method of co-extrusion or lamination with a thermoplastic resin and different thermoplastic resin or another material

intrinsically having no adhesiveness to the thermoplastic resin by use of no adhesive.

Firstly, the method of the treatment of a thermoplastic resin according to the present invention comprises subjecting the thermoplastic resin to a vacuum plasma treatment at a temperature equal to or higher than the melting or softening point of the resin.

Secondly, the method for the preparation of a laminated material according to the present invention comprises subjecting a thermoplastic resin to a vacuum plasma treatment at a temperature equal to or higher than the melting or softening point of the resin and laminating the thus plasma-treated thermoplastic resin with another material which is a different material from the thus plasma-treated thermoplastic resin.

#### BREIF DESCRIPTION OF THE DRAWING

FIGURES 1 and 2 are each a schematic illustration of an example of the apparatus used for practicing the vacuum plasma treatment according to the first aspect of the invention.

FIGURES 3 and 4 are each a schematic illustration of the process of melt-kneading according to another embodiment of the inventive method.

FIGURE 5 is a schematic illustration of an example of the apparatus for practicing the method for the preparation of a laminated body according to the second embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The thermoplastic resins to which the inventive method is applicable are not particularly limitative including, for example, crystalline polyolefins such as high-density polyethylene, low-density polyethylene, polypropylene, copolymers of two kinds or more of olefins, copolymers of ethylene and acrylic acid, copolymers of ethylene and vinyl acetate, copolymers of ethylene and vinyl alcohol and the like; low crystalline or non-crystalline polyolefins such as copolymers of ethylene and propylene, copolymers of ethylene and butene-1 and the like; polyesters; polycarbonate; polyamides; styrene-based resins such as general-purpose polystyrenes, high-impact polystyrenes, AS resins, ABS resins and the like; polyvinyl chloride; polyvinylidene chloride; polyvinyl alcohol; acrylic resins; and others. These thermoplastic resins may be used either singly or as a blend of two kinds or more according to need. When two kinds or more of the resins are used in combination, the compatibility thereof is of no particular criticality and incompatible resins may be used in combination. It is further optional that the thermoplastic resin is admixed with conventional additives including various kinds of stabilizers against oxidation, heat, light, etc., fillers such as calcium carbonate, talc, clay, silica, etc., reinforcing materials such as glass fibers, carbon fibers, metal fibers, organic fibers, etc., rubbers, lubricants, antistatic agents, plasticizers, coloring materials, e.g. titanium dioxide, and others each in a suitable amount.

In the method of the present invention, the temperature at which the vacuum plasma treatment is performed should be equal to or higher than the melting point when the thermoplastic resin is crystalline or the softening or glass transition point when the resin is non-crystalline. The actual conditions for practicing the treatment according to the invention are not particularly limitative excepting the above mentioned temperature condition. For example, the treatment may be effected on the film-like body in a molten state immediately after the melt extrusion and prior to cooling or may be effected on the resin once cooled and then reheated up to the above mentioned temperature. Alternatively, the vacuum plasma treatment may be performed when the molten resin is under continuous kneading. The treatment of sheets, films and other ready-shaped articles should be performed by increasing the surface temperature thereof up to the above mentioned temperature with a suitable outer heating means. The treatment may be carried out either in a continuous process or in a batch-wise process.

The actual temperature of the thermoplastic resin under the vacuum plasma treatment should be adequately selected in consideration of the type of the resin, form of the shaped article, molding method, conditions of the treatment and other factors although it is preferable that the temperature is from 5 to 10°C higher than the melting or softening point of the resin as a general guideline.



The vacuum plasma here implied is a non-equilibrium plasma obtained by the activation of gas molecules with glow discharge, radio frequency discharge, microwave discharge and the like. The vacuum plasma treatment of a thermoplastic resin is performed by exposing the resin to the plasma atmosphere generated by the electric discharge under a pressure not exceeding 100 Torr or, usually, in the range from 0.005 to 20 Torr or, preferably, in the range from 0.02 to 5 Torr or, alternatively, by blowing the plasma at the resin to be treated. The length of time for the treatment is not particularly limitative although a time of 1 second to 10 minutes is usually sufficient.

Examples of the gas which can be used for gas plasma at the vacuum plasma treatment are a non-polymer-forming gas such as air, oxygen, nitrogen, hydrogen, argon, helium, xenon, carbon dioxide, nitrous oxide, nitrogen monoxide, nitrogen dioxide and the like or a polymer-forming gas such as methane, ethane, ethylene, acetylene, benzene, tetrafluoroethylene, tetramethyl silane, tetramethyl tin, acrylonitrile and the like. These gases may be used as a mixture of two kinds or more according to need. Selection of the gas should be dependent on the kind of the resin under treatment, the object of the plasma treatment and other factors.

The conditions of the vacuum plasma treatment according to the invention include no particular limitations excepting the temperature which should be equal to or higher than the melting or softening point of the thermoplastic resin as

the material of the article under treatment. In a procedure, for example, the thermoplastic resin is put into the plasma chamber which is then evacuated to an appropriate pressure and, while the resin is heated before or after evacuation to a desired temperature and kept at the temperature, a gas is introduced into the chamber followed by the glow discharge or other electric discharge to generate plasma to which the resin is exposed. A very high efficiency of the treatment is obtained in this manner because the treatment is effected on the thermoplastic resin in a highly active state at the melting or softening point of the resin or higher so that the thus treated resin is imparted with excellent properties. The method of the invention can be performed satisfactorily by use of a conventional apparatus for the vacuum plasma treatment merely with control of the temperature of the resin within the specified range but the characteristic features of the inventive method are clearer when the treatment is performed according to the procedure described below.

In particular, the preferable procedures include the treatment of an extruded resin film in a molten or softened state immediately after melt extrusion before cooling and solidification and the treatment of the resin while it is molten and under continuous kneading. These methods are advantageous owing to the use of a simple apparatus and the high efficiency of the treatment.

In the following, an embodiment of the treating method according to the invention is described in detail with

reference to FIGURES 1 and 2 illustrating an example of the apparatus for the continuous treatment.

As is shown in FIGURE 1, the extrusion die 4 of an extrusion molding machine 3 is mounted on the inlet port 2 of the chamber for vacuum plasma treatment 1 in a vacuum-tight condition. The thermoplastic resin loading the extrusion molding machine 3 is extruded out of the extrusion die 4 and directly introduced into the plasma treatment chamber 1. The sheet or film of the resin 5 shaped at the extrusion die 4 as it is introduced into the plasma treatment chamber 1 is subjected to the vacuum plasma treatment in the chamber 1 before the resin is cooled and solidified. The plasma treatment chamber per se can be any one of known types. As is illustrated in the figure, for example, the chamber 1 is provided with a pair of electrodes 6, 6', a gas exhaust tube 7 and a gas inlet tube 8. While the plasma treatment chamber 1 is evacuated by pumping through the gas exhaust tube 7, a gas such as air, oxygen, argon, nitrous oxide and the like is introduced into the chamber 1 from the gas inlet tube 8. The vacuum plasma treatment of the sheet or film of the thermoplastic resin 5 is performed by generating plasma with electric discharge between the electrodes 6, 6' while the sheet or film is running between the electrodes. The resin sheet or film 5 after the plasma treatment is cooled by the cooling roller 9 and then taken up on the winding-up unit 10.

FIGURE 2 is an illustration of another apparatus usable for the treatment according to the invention.

The resin sheet or film 5 after the plasma treatment in the same manner as above is led through the exit 11 of the plasma treatment chamber 1 and introduced into the preparatory vacuum chamber 12 which is connected to the exit 11 of the plasma treatment chamber 1 in a vacuum-tight condition.

The preparatory vacuum chamber per se can also be any one of known types and constructed, for example, of several sealing chambers 12a, 12b, 12c, ..... each composed of a housing and a pair of sealing rollers facing up and down.

The resin sheet or film 5 runs through the sequence of these sealing chambers in series each under a stepwise increasing pressure and is led to the atmosphere out of the last-positioned sealing chamber which is under a pressure approximating the atmospheric to be taken up on the winding-up unit 10. The apparatus illustrated in FIGURE 2 provides a possibility of a continuous treatment over a further extended length of time.

According to the above described embodiment of the inventive treating method, the thermoplastic resin is directly introduced into the plasma treatment chamber as it is extrusion-molded out of the extrusion die of the extrusion molding machine so that the surface of the resin sheet or film before or under the treatment is still in a highly active state at a temperature equal to or higher than the melting or softening point of the resin and also in a clean condition without deposition of dusts, dirt, fungi and the like so that the vacuum plasma treatment can be performed with a very high efficiency of the

treatment can be performed with a very high efficiency of the treatment if not to mention the excellent sanitariness of the surface. Moreover, the method of the invention for the preparation of a laminated material provides a possibility of obtaining an unexpectedly high adhesive bonding as is described later by utilizing the surface at an elevated temperature activated by the vacuum plasma treatment. In addition, the inventive treating method is economically advantageous owing to the energy saving achieved by the omission of reheating of the resin sheets or films according to an embodiment of the invention and reduction of the investment for the apparatus which is provided only a single sealing means between the vacuum plasma treatment chamber and the atmospheric air along with the possibility of conducting the method in a continuous process thus contributing to the reduction of the overall cost for the treatment. The inventive method is also a method with an extremely high productivity since a sheet-like material of the thermoplastic resin imparted with excellent surface properties can be produced continuously in a continued sequence of the extrusion molding and the surface treatment without break.

In the following, a detailed description is given with reference to FIGURES 3 and 4 of the method for the vacuum plasma treatment of a thermoplastic resin under continuous melt-kneading as an embodiment of the invention.

The plasma treatment of a resin under melt-kneading can be performed either in a batch-wise process illustrated in FIGURE 3 or in a continuous process illustrated in FIGURE 4. In the apparatus illustrated in FIGURE 3, a double-roll mill 22 is installed inside the vacuum plasma treatment chamber 1 and the plasma treatment is performed by the generation of plasma inside the chamber using the electrode 6 and the radio frequency generator 21 while the thermoplastic resin 23 is under milling in a molten state on the double-roller mill 22. The double-roller mill as the kneading machine may be replaced with a Banbury mixer or the like blending machine. The apparatus illustrated in FIGURE 4 is an extruder machine in which the thermoplastic resin is plasma-treated on the way in the kneading cylinder. The extruder machine can be a single-screw extruder, multi-screw extruder, disk extruder or the like. The effect of the plasma treatment performed under such a melt kneading is not limited to the surface of the resin but high uniformity is obtained of the effect throughout the whole volume of the resin which can be directly molded into a shaped article such as a sheet or may shaped into pellets and the like intermediate form for the resin molding. When the plasma treatment of a resin under melt kneading is performed with simultaneous compounding with a filler, reinforcing material and the like additives, the interfacial adhesion between the resin and the surface of these additives is remarkably improved so that the articles shaped of such a resin blend can be

imparted, in particular, with excellent mechanical properties.

As is described above in detail, the vacuum plasma treatment of the inventive method is performed at a temperature equal to or higher than the melting or softening point of the thermoplastic resin, which has been developed on the base of an idea quite different from that in the conventional plasma treatment carried out at a temperature lower than that and not capable of achieving the object in the present invention. Besides, the effectiveness of the inventive method is not limited to the very surface of the resin article but can reach the inside of the surface layer to some extent and even good uniformity of the effect of the treatment can be obtained over whole volume of the resin according to the plasma treatment of the resin under melt kneading as is described above.

Different from the conventional methods, the effect of the treatment according to the inventive method is much superior and the resin articles can be imparted with remarkably improved surface properties such as the susceptibility to adhesive bonding, paintability, plating adaptability, printability, antistatic performance and the like. In particular, a great improvement is obtained in the strength of adhesive bonding enabling lamination of a non-adhesive resin along with a possibility of obtaining a resin blend having excellent properties in compounding an incompatible resin, filler, reinforcing material and the like.

In the next place, the second aspect of the present invention relates to a method for the preparation of a laminated material by use of the thermoplastic resin having been plasma-treated according to the above described first aspect of the invention. That is, the method for the preparation of a laminated material comprises subjecting a thermoplastic resin to a vacuum plasma treatment at a temperature equal to or higher than the melting or softening point of the resin and laminating the thus vacuum plasma-treated thermoplastic resin with a material other than the thermoplastic resin.

The thermoplastic resin usable in this process is not particularly limitative and can be any one of those named before. The material to be laminated with the plasma-treated thermoplastic resin is, on the other hand, exemplified by thermoplastic resins other than the vacuum plasma-treated resin; metals such as aluminum, iron, copper and the like; thermosetting resins such as FRP and the like; cellulosic resins such as cellophane and the like; papers; woven and non-woven cloths; rubbers; woods; ceramics such as glass, porcelain and the like; and others. Lamination is not limited to a single layer of one of these materials but 2 layers or more can be laminated. The form of the laminated layer is also not limitative including, in the case of a metal, for example, metal foils, vapor-deposited films of the metal, metal plates, metal tubes and other forms.



The combinations of the base materials for the preparation of the laminated material can be selected according to the particular object including a combination of two different thermoplastic resins and combination of a thermoplastic resin and another material of a different kind such as a metal. The number of the laminated layers can be 2 or 3 or more according to need.

The thermoplastic resin used here can be a blend of two kinds or more of thermoplastic resins and may be admixed with various kinds of additives including fillers, e.g. calcium carbonate, talc, clay and the like, rubbers, reinforcing materials, plasticizers, stabilizers and others each in an adequate amount.

The process of lamination is generally carried out by overlaying the plasma-treated surface of the thermoplastic resin with another base material to be laminated thereon and bonding them together under pressure, if necessary, with heating. In this case, it is optional if desired that the surface of the latter material is also subjected to the vacuum plasma treatment and the thus plasma-treated surfaces of the two materials are contacted together and bonded under a pressure to effect lamination. In some cases, the vacuum plasma treatment is not performed over whole surface area of the material but performed only on a part of the surface area. For example, the vacuum plasma treatment in the preparation of a multilayered laminated body is performed on the surface of a sheet material leaving the peripheral portions untreated and

such peripheral portions conventionally discarded by trimming but untreated and hence unbonded in this case can readily be recovered and recycled to the next use after reclaiming.

The procedure for the lamination is not particularly limitative and can be performed either continuously following the vacuum plasma treatment or batch-wise. For example, the lamination can be performed continuously in the plasma treatment chamber for the above mentioned vacuum plasma treatment or performed immediately following the exit of the material out of the vacuum treatment chamber. When the vacuum plasma treatment is performed during the melt-kneading of the thermoplastic resin, the lamination can be performed either inside the die or outside the die. Alternatively, the thermoplastic resin plasma-treated during melt-kneading can be used for lamination as a film adhesive after film forming in advance or lamination is performed by the technique of extrusion coating. Further, it is of course optional to perform the lamination by reheating a once cooled thermoplastic resin after the vacuum plasma treatment with another material. In particular, the procedure of lamination carried out within the vacuum plasma treatment chamber is advantageous because the adhesive bonding takes place in a highly active plasma atmosphere free from moisture, dusts and the like foreign materials so that the laminated material prepared in such a procedure is imparted with a further improved adhesive bonding strength between layers. It is optional in carrying

out the lamination to use an adhesive according to need.

As is described above, the object of the present invention can be achieved by the vacuum plasma treatment of the thermoplastic resin only when the temperature at the treatment is equal to or higher than the melting or softening point of the resin and no satisfactory results can be obtained by the vacuum plasma treatment at a lower temperature.

FIGURE 5 is a schematic illustration of an apparatus for suitably performing continuous preparation of a laminated material according to the second aspect of the present invention. The thermoplastic resin molten and kneaded in the extruder 3 is extruded in a sheet like form 5 and led into the space between the electrodes 6, 6' in the vacuum plasma treatment chamber 1 where it is subjected to the vacuum plasma treatment. Another intrinsically non-adhesive thermoplastic resin is extruded out of a second extruder 3' in a sheet like form 5' and these two sheets 5, 5' are adhesively bonded together into a laminate by passing a pressure roller 13 followed by cooling on a cooling roller 9. The laminated material is led out of the chamber 1 through a preparatory vacuum chamber 12 and taken up on a winding-up unit 10. Apart from the illustration in FIGURE 5 in which the sheet 5' of the second thermoplastic resin is laminated without being subjected to the vacuum plasma treatment, it is particularly preferable that the second resin sheet 5' is also subjected to the vacuum plasma treatment at a temperature equal to or higher than the melting or softening point of the resin.

As is understood from the above description, the second aspect of the present invention provides a means for obtaining a laminated material having an extremely high adhesive bonding strength between layers even without using an adhesive. The efficiency of the treatment is particularly high when the lamination is performed at an elevated temperature of the laminated sheets still in the highly active plasma atmosphere. Different from conventional methods such as the co-extrusion multilayer molding, lamination molding and the like, a laminated material can be prepared without using an adhesive resin such as modified polyolefins or an adhesive such as urethane and epoxy based ones and the process of lamination requires no complicate extrusion and coating machines as well as no working steps therefore so that the overall costs for lamination can be much lower than in the conventional methods.

Accordingly, the laminated material obtained in this manner is a material having a composite of the excellent properties possessed by the respective base materials such as low oxygen permeability, low moisture permeability, printability, heat-sealability, mechanical strength, resistance against chemicals, corrosion resistance, electric conductivity and the like. The laminated materials according to the invention are useful as a wrapping and packaging material, industrial material, building material and others.

In the following, the present invention is described in more detail by way of examples.

Example 1

A sheet of a GP-grade polystyrene having a melt index of 3.8 g/10 minutes and a glass transition point of 80°C was held in a vacuum plasma treatment chamber and heated to 210°C and the chamber was evacuated to a pressure of  $1 \times 10^{-2}$  Torr while the resin sheet was kept at the above temperature. Then, nitrogen gas was passed through the chamber at a rate of 50 ml/minute to control the pressure inside the chamber at 1 Torr and the vacuum plasma treatment of the resin sheet was performed for 60 seconds by supplying a discharge power of 50 watts output.

The contact angle of water on the surface of the thus treated resin sheet was 39° which was much smaller than the corresponding value of 86° before the treatment indicating a great increase in the hydrophilicity of the surface.

Example 2

A sheet of a high density polyethylene having a density of 0.965 g/cm<sup>3</sup>, melt index of 14 g/10 minutes and melting point of 131°C in place of the GP polystyrene sheet was subjected to the vacuum plasma treatment in substantially the same manner as in Example 1 except that the temperature of the resin sheet during the treatment was 190°C.

The contact angle of water on the thus treated surface was 61° while the value was 100° before the treatment.

Example 3

A sheet of a high density polyethylene having a density

of 0.967 g/cm<sup>3</sup>, melt index of 5.8 g/10 minutes and melting point of 136°C in place of the GP polystyrene sheet was subjected to the vacuum plasma treatment in substantially the same manner as in Example 1 except that the temperature of the resin sheet during the treatment was 170°C and the length of time for the treatment was 10 seconds.

The contact angle of water on the thus treated surface was 68° while the value was 95° before the treatment.

#### Comparative Example 1

Substantially the same experimental procedure as in Example 3 was repeated except that the temperature of the resin sheet during the vacuum plasma treatment was 127°C. The contact angle of water on the thus plasma-treated surface of the resin sheet was 78° and this value changed only slightly to 77° when the resin sheet was subsequently heated at 170°C.

#### Comparative Example 2

The experimental procedure was substantially the same as in Example 3 except that the temperature of the resin sheet was 30°C to give a contact angle of water of 95° after heating at 170°C.

#### Examples 4 to 8

Sheets of two different kinds of thermoplastic resins A and B indicated in Table 1 below were each held in a vacuum plasma treatment chamber and heated at a temperature

also indicated in the same table and then the chamber was evacuated to a pressure of  $1 \times 10^{-2}$  Torr while the resin sheets were kept at the respective temperatures. Nitrogen gas was passed through the chamber at a rate of 50 ml/minute to control the pressure inside the chamber at 1 Torr and the vacuum plasma treatment of the resin sheets was performed for 60 seconds by supplying a discharge power of 50 watts output. Thereafter, the thus plasma-treated resin sheets A and B were laid one on the other in such a manner that the plasma-treated surfaces were in direct contact with each other in the plasma treatment chamber and bonded together under pressure to prepare a laminated material. The thus prepared laminated material was subjected to the test of the peeling resistance between the base sheets by 180° pulling at the bonded portion. The results are shown in Table 1 together with the comparative data obtained with similar laminated materials prepared without the treatment. In Table 1, the types of the thermoplastic resins are given by the following abbreviations.

EVOH: a copolymer of ethylene and vinyl alcohol containing 40% by weight of ethylene; density  $1.19 \text{ g/cm}^3$ ; melt index 1.5 g/10 minutes; melting point  $181^\circ\text{C}$ .

PC: a polycarbonate resin having an average molecular weight of 22,000; glass transition point  $147^\circ\text{C}$ .

GP-PS: a GP-grade polystyrene; melt index 3.8 g/10 minutes; glass transition point  $80^\circ\text{C}$ .

PP: a random copolymer of propylene and ethylene containing 4% by weight of ethylene; melt index 7.0 g/10

minutes; melting point 155°C.

EVA: a copolymer of ethylene and vinyl acetate containing 20% by weight of vinyl acetate; density 0.939 g/cm<sup>3</sup>; melt index 20 g/10 minutes; melting point 92°C.

LDPE: a low density polyethylene; density 0.921 g/cm<sup>3</sup>; melt index 4 g/10 minutes; melting point 111°C.

HDPE: a high density polyethylene; density 0.955 g/cm<sup>3</sup>; melt index 0.05 g/10 minutes; melting point 130°C.

Table 1

Example No.	Thermoplastic resin				Peeling resistance, g/15 mm	
	A		B		Treated	Untreated
	Type	Temperature °C	Type	Temperature °C		
4	EVOH	210	PP	220	650	20
5	EVOH	210	EVA	150	2100	520
6	EVOH	210	LDPE	190	1600	20
7	PC	250	LDPE	190	1300	20
8	GP-PS	210	HDPE	190	280	30

Comparative Example 3

A laminated material was prepared in substantially the same manner as in Example 4 except that the vacuum plasma treatment was performed at 25°C of the resin sheets followed by heating thereof at 220°C. The peeling resistance of this laminated material by 180° pulling was 60 g/15 mm.



#### Comparative Example 4

A laminated body was prepared in substantially the same manner as in Example 4 except that the vacuum plasma treatment was performed at 120°C of the resin sheets followed by heating thereof at 220°C. The peeling resistance of this laminated material by 180° pulling was 70 g/15 mm.

#### Example 9

The experimental procedure was substantially the same as in Example 4 but the thermoplastic resins A and B were a copolymer of ethylene and vinyl acetate and a 95:5 by weight resin blend of a polypropylene and a copolymer of ethylene and vinyl acetate, respectively, and the vacuum plasma treatment was performed for 3 seconds at a temperature of 215°C with carbon dioxide as the gas in place of nitrogen. The peeling resistance of the thus obtained laminated material by 180° pulling was 1200 g/15 mm.

#### Example 10

The experimental procedure was just the same as in Example 9 except that the gas was nitrous oxide  $N_2O$  in place of carbon dioxide. The peeling resistance of the thus obtained laminated material by 180° pulling was 1100 g/15 mm.

#### Example 11

The experimental procedure was about the same as in Example 4 except that the vacuum plasma treatment was

performed for 3 seconds at a temperature of 215°C with nitrous oxide as the gas in place of nitrogen. The peeling resistance of the thus obtained laminated material by 180° pulling was 1600 g/15 mm.

#### Example 12

The experimental procedure was substantially the same as in Example 4 but the thermoplastic resins A and B were a copolymer of ethylene and vinyl acetate and a 99:1 by weight polymer blend of a polypropylene and an ethylene-propylene elastomer containing 26% by weight of propylene and having a Mooney viscosity of  $ML_{1+4}$  100°C 70, respectively, and the vacuum plasma treatment was performed for 3 seconds at a treatment temperature of 215°C with nitrous oxide as the plasma supporting gas in place of nitrogen. The peeling resistance of the thus obtained laminated material by 180° pulling was 1800 g/15 mm.

#### Example 13

The experimental procedure was substantially the same as in Example 13 except that the thermoplastic resin B was a 79:20:1 by weight blend of a polypropylene, a low density polyethylene having a density of 0.919 g/cm<sup>3</sup> and a melt index of 1 g/10 minutes and titanium dioxide. The peeling resistance of the thus obtained laminated material by 180° pulling was 3000 g/15 mm.

Example 14

A 200  $\mu\text{m}$  thick film of a high density polyethylene having a density of  $0.955 \text{ g/cm}^3$ , melt index of 0.05 g/10 minutes and melting point of  $130^\circ\text{C}$  and a 1 mm thick aluminum plate were each held in a vacuum plasma treatment chamber and heated at  $200^\circ\text{C}$  and the chamber was evacuated to a pressure of  $1 \times 10^{-2}$  Torr while the film and the plate were kept at the above mentioned temperature. Oxygen gas was passed through the chamber at a rate of 50 ml/minute to control the pressure inside the chamber at 1 Torr and the surface of the polyethylene film was subjected to a vacuum plasma treatment for 20 seconds by supplying a discharge power of 50 watts output. Thereafter, the polyethylene film and the aluminum plate were laminated by press-bonding with the plasma-treated surface of the resin film as the bonding surface. The peeling resistance of the thus obtained laminated material by  $180^\circ$  pulling was 1600 g/15 mm.

Example 15

The plasma-treated polyethylene film obtained in Example 14 was cooled to  $50^\circ\text{C}$  and then reheated at  $200^\circ\text{C}$  before it was laminated with the aluminum plate in the same manner as in Example 14. The peeling resistance of the thus obtained laminated material by  $180^\circ$  pulling was 100 g/15 mm.

Comparative Example 5

Lamination was tried with the same polyethylene film and aluminum plate as used in Example 14 by press-bonding at 200°C without performing the vacuum plasma treatment only to find that no adhesive bonding took place at all between them.

Comparative Example 6

A laminated material was prepared in just the same manner as in Example 14 except that the vacuum plasma treatment was performed at room temperature instead of 200°C. The peeling resistance of the thus obtained laminated material by 180° pulling was 30 g/15 mm.

Example 16

The experimental procedure was substantially the same as in Example 14 except that the aluminum plate was replaced with a glass plate which was a slide glass used for optical microscopy. The peeling resistance of the thus obtained laminated material of the polyethylene film and glass plate by 180° pulling was 2400 g/15 mm.

Example 17

The experimental procedure was substantially the same as in Example 16 except that the polyethylene film after the vacuum plasma treatment was cooled to 50°C and then reheated at 200°C before it was laminated with the glass plate. The peeling resistance of the thus obtained

laminated material by 180° pulling was 500 g/15 mm.

Comparative Example 7

Lamination was tried with the same polyethylene film and glass plate as used in Example 16 by press-bonding at 200°C without performing the vacuum plasma treatment only to find that no adhesive bonding took place at all between them.

WHAT IS CLAIMED IS:

1. A method for the treatment of a thermoplastic resin which comprises subjecting the thermoplastic resin to a vacuum plasma at a temperature equal to or higher than the melting or softening point of the resin.
2. The method as claimed in Claim 1, wherein the vacuum plasma treatment of the thermoplastic resin is performed directly as the thermoplastic resin is extruded out of the die of an extrusion molding machine and introduced into a vacuum plasma treatment chamber.
3. The method as claimed in Claim 1, wherein the vacuum plasma treatment of the thermoplastic resin is performed as the thermoplastic resin is kneaded in a molten state.
4. The method as claimed in Claim 1, wherein the temperature of the thermoplastic resin under the vacuum plasma treatment is 5 to 10°C higher than the melting or softening point of the resin.
5. The method as claimed in Claim 1, wherein the thermoplastic resin is a compound selected from the groups consisting of high-density polyethylene, low-density polyethylene, polypropylene, copolymers of ethylene and acrylic acid, copolymers of ethylene and vinyl acetate, copolymers of ethylene and vinyl alcohol, copolymers of ethylene and propylene, copolymers of ethylene and

butane-1, polyesters, polycarbonate, polyamides, general purpose polystyrenes, high-impact polystyrenes, AS resins, ABS resins, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol and acrylic resins.

6. The method as claimed in Claim 1, wherein the vacuum plasma treatment of the thermoplastic resin is performed under a pressure in the range from 0.005 to 20 Torr.

7. The method as claimed in Claim 1, wherein the vacuum plasma treatment of the thermoplastic resin is performed by using gas selected from the groups consisting of air, oxygen, nitrogen, hydrogen, argon, helium, xenon, carbon dioxide, nitrous oxide, nitrogen monoxide, nitrogen dioxide, methane, ethane, ethylene, acetylene, benzene, tetrafluoroethylene, tetramethyl silane, tetramethyl tin and acrylonitrile.

8. A method for the preparation of a laminated material which comprises subjecting a thermoplastic resin to a vacuum plasma treatment at a temperature equal to or higher than the melting or softening point of the resin and laminating the thus vacuum plasma-treated thermoplastic resin with another material which is a different material from the thermoplastic resin.

9. The method as claimed in Claim 8, wherein the material different from the thermoplastic resin is selected from the group consisting of thermoplastic resins different

from the vacuum plasma-treated thermoplastic resin, thermosetting resins, cellulosic resins, papers, woven cloths, non-woven cloths, rubbers, metals, woods and ceramics.

10. The method as claimed in Claim 8, wherein the temperature of the thermoplastic resin under the vacuum plasma treatment is 5 to 10°C higher than the melting or softening point of the resin.

11. The method as claimed in Claim 8, wherein the thermoplastic resin is a compound selected from the groups consisting of high-density polyethylene, low-density polyethylene, polypropylene, copolymers of ethylene and acrylic acid, copolymers of ethylene and vinyl acetate, copolymers of ethylene and vinyl alcohol, copolymers of ethylene and propylene, copolymers of ethylene and butane-1, polyesters, polycarbonate, polyamides, general purpose polystyrenes, high-impact polystyrenes, AS resins, ABS resins, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol and acrylic resins.

12. The method as claimed in Claim 8, wherein the vacuum plasma treatment of the thermoplastic resin is performed under a pressure in the range from 0.005 to 20 Torr.

13. The method as claimed in Claim 8, wherein the vacuum plasma treatment of the thermoplastic resin is performed by using gas selected from the groups consisting



of air, oxygen, nitrogen, hydrogen, argon, helium, xenon, carbon dioxide, nitrous oxide, nitrogen monoxide, nitrogen dioxide, methane, ethane, ethylene, acetylene, benzene, tetrafluoroethylene, tetramethyl silane, tetramethyl tin and acrylonitrile.

FIG. 1

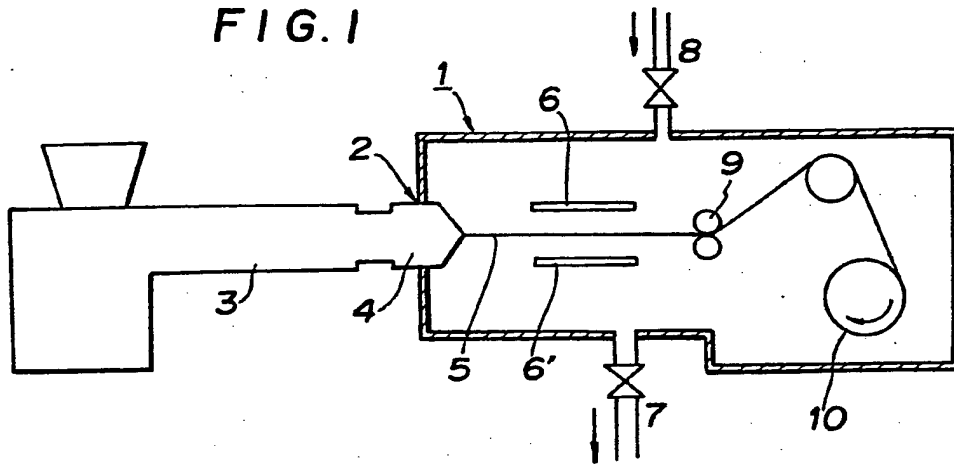


FIG. 2

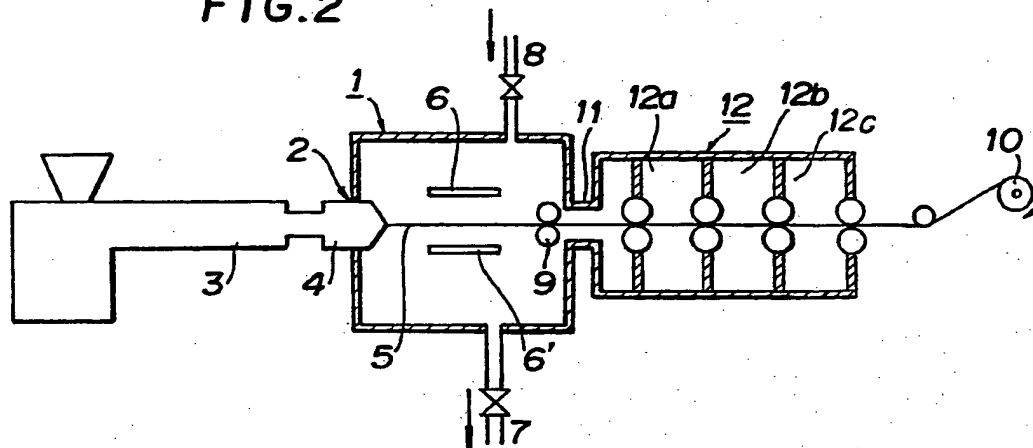


FIG. 3

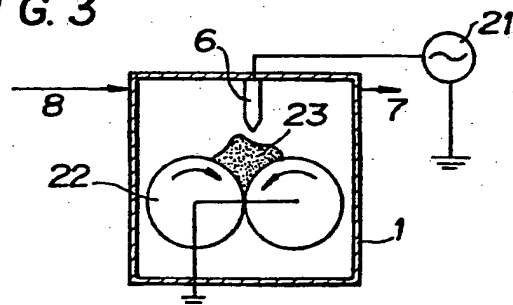


FIG. 4

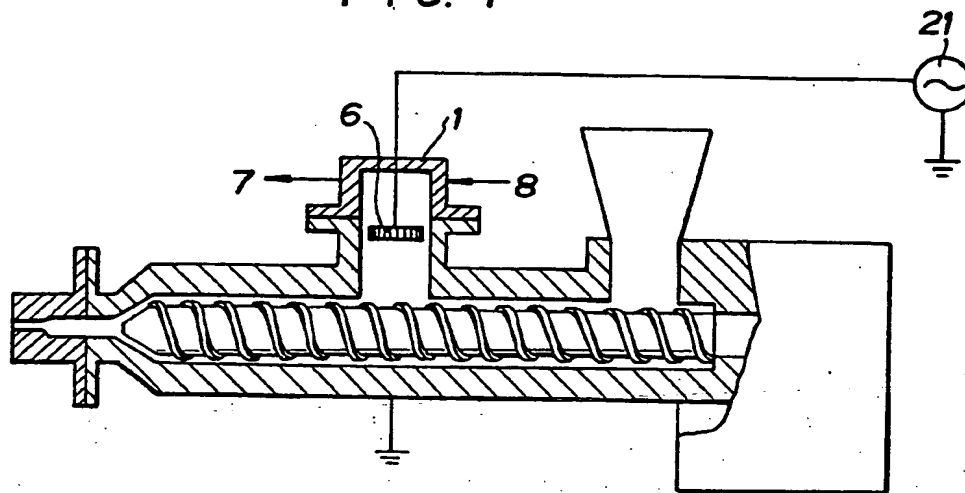
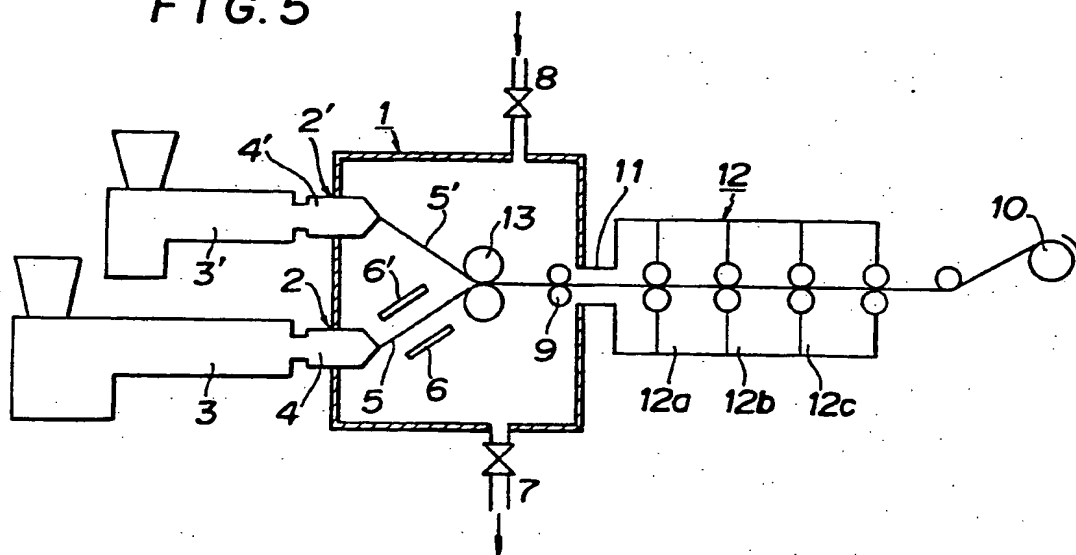


FIG. 5



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